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PRODUCTS HAVING MULTIPLE-SUBSTITUTED
POLYSILOXANE MONOLAYER

The present invention relates to providing

5 specialized polysiloxane coatings to articles. The coatings provide protective attributes to the substrates bearing the coatings, without loss of and in some cases with enhancement of the desirable properties of the substrates.

10 The present invention relates in particular to the formation of specialized siloxane monolayers on substrates which are susceptible to damage upon exposure to acidic environments or basic environments, or which are vulnerable to physical degradation such as cracking.

15 The invention relates in particular to the provision of such monolayers on silica-based chromatographic supports, in order to protect such supports from damage due to the ambient chemical environment while retaining the desirable chromatographic properties of the support.

20 The invention also relates to providing such monolayers to glassware and glass surfaces, to provide desired protection as described hereinbelow.

While it has generally been known to apply "silicone" coatings to articles to impart various
25 protective properties, such as waterproofing, it is believed herein to be novel to adjust the substituents on the silicon atoms making up such coatings in order to favorably affect the properties of the coating and of the articles bearing the coating. In addition,
30 providing such adjustment on "coatings" which are in reality monolayers of siloxanyl (that is, -Si-O-) based monolayers is believed to be all the more novel.

1 Chromatographic packings can comprise silica
gel to which organic substituents, such as alkyl chains,
have been attached. It has heretofore been accepted
that the susceptibility of such materials to attack by
5 acids or bases has been an unavoidable concomitant of
the packing's ability to perform properly in
chromatographic applications. Thus, modification such
as that which is the subject of the present invention
has not been considered.

10 Indeed, formation of a siloxanyl monolayer
might be expected to interfere with properties such as
chromatographic capabilities because it would alter the
shape and size of pores and would affect other surface
characteristics.

15 For instance, a published abstract with
respect to Japanese Patent Application No. 61287444
describes porous silica particles characterized in that
the inner surfaces of the pores carry a hydrophobic
layer formed by a reaction of the silica in the pore
20 with an alkyl or aryl halosilane, among which are listed
octadecyltri-chlorosilane and propyltrichlorosilane,
among others, wherein the remaining exposed surface of
the silica particle is bonded to hydrophilic groups such
as ethylene glycol, glycerol, sorbitol, polyethylene
25 oxide, glycidoxypropyltrimethoxy-silane,
ethyleneglycolmono-ethylether, or diethyleneglycol. The
abstract does not disclose the formation of a siloxanyl
monolayer, nor is there disclosed any intimate
intermingling of different substituents on adjacent
30 silicon atoms; indeed, such a product would be directly
contrary to the teachings of this abstract which

1 requires substituents of various types at quite distinct
locations on the silica particle.

A number of other sources disclose bonding
various substituents to an oxide surface, particularly a
5 silica surface, but none discloses or suggests providing
multiple distinct substituents at adjacent or nearly
adjacent sites on a siloxanyl monolayer. Examples
wherein the substrate is glass or a chromatographic
surface include U.S. Defensive Publication T958,010,
10 U.S. Patent No. 4,755,294, U.S. Patent No. 4,604,207,
and U.S. Patent No. 4,512,898. Other publications
examining the formation of alkyl-substituted siloxanyl
monolayers on silica gel are typified by P. Silberzan,
et al., in Langmuir, Vol. 7, No. 8, pp. 1647-1651 (1991)
15 and S. Wasserman, et al., in J. Am. Chem. Soc., Vol.
111, No. 15, pp. 5852-5861 (1989).

Briefly stated, one aspect of the present
invention is a product to which is chemically bonded a
monolayer of silicon atoms which are connected to other
20 silicon atoms in said monolayer through oxygen atoms in
said monolayer, wherein the monolayer is substituted
with a first hydrocarbyl substituent and a second
hydrocarbyl substituent and each of the silicon atoms in
said monolayer is substituted with said first
25 hydrocarbyl substituent or said second hydrocarbyl
substituent, wherein said first hydrocarbyl substituent
is longer than said second hydrocarbyl substituent.

In another aspect of the present invention,
the product is silica gel or another inorganic oxide, or
30 a substrate whose surface is silica gel or such other
inorganic oxide, and the first and second hydrocarbyl
substituents are selected such that the substrate

1 bearing the substituted monolayer is useful as, for
instance, a chromatography column, and exhibits a high
degree of resistance to acidic and basic attack. Yet
another aspect of the present invention is the use of
5 such a product in chromatography.

Yet another aspect of the present invention is
glass, such as glass articles, glassware, glass optical
fibers, glass capillaries, and the like, bearing the
monolayer described herein, wherein the monolayer
10 protects the surface of the glass from acidic and basic
environments and from physical degradation such as
cracking.

While the present invention is particularly
useful in the preparation of products comprising silica
15 which bears the monolayer described herein, the present
invention is believed to be useful in providing the
indicated protection against chemical degradation to a
large variety of materials. Stated generally, any
product having a surface which reacts with alkyl
20 trichlorosilane to bond to the silane, can be provided
with a monolayer in accordance with the present
invention. Preferred materials are characterized in
that they comprise surface oxygen. By "surface oxygen"
is meant that the material contains, at its surface,
25 oxygen which is covalently (or, in certain embodiments,
ionically) bound in the material, which oxygen is
capable of being covalently bonded to silanes. More
specifically, the surface oxygen is considered within
the scope of this aspect of the invention if the oxygen
30 reacts with any alkyl trichloro-silane to form O-Si
bonds.

1 Preferred materials to which the monolayer is
applied include silica gel, silica-based glass and
glassware, and optical "fiber optic" cable, as well as
materials comprising oxides or mixed oxides of any
5 inorganic material whose oxide is solid at standard
temperature and pressure. Also included are carbonates,
aluminosilicates, silicates and phosphates, of any
inorganic cation. Also included are materials in which
two or more of these are chemically combined or
10 physically blended. Examples of the foregoing include
inorganic pigments, limestone and clays (which typically
comprise aluminosilicates). Additional examples include
any inorganic element and oxides thereof so long as the
surface thereof is capable of forming bonds to silicon
15 atoms in the monolayer. Examples include but are not
limited to alumina, zirconia, beryllia, titanium
dioxide, magnesium oxide, and oxides of vanadium,
chromium, manganese, iron, cobalt, nickel, copper, zinc,
gadolinium, germanium, arsenic, rubidium, strontium,
20 yttrium, niobium, molybdenum, ruthenium, rhodium,
platinum, gold, silver, thallium, lead and bismuth.

One preferred embodiment of the present
invention is silica gel or a substrate of a different
material having a silica gel surface. The monolayer
25 provides a protective layer to the silica gel.

The invention finds particular usefulness in
chromatographic applications, including not only silica-
based chromatographic supports but also metal-oxide
chromatographic substrates.

30 Another preferred embodiment of the present
invention is glass articles, such as glassware,
capillary tubes, optical fibers, windows and windshields

1 (whether for conventional construction and vehicular
applications or more specialized uses in reactors and
spacecraft), and any other article having a glass outer
and/or inner surface. Providing the monolayer to
5 glassware will help protect against acidic and basic
environments, and will help resist the microscopic
chemical and mechanical processes at the glass surface
that help initiate and propagate cracking and related
degradation. Providing the monolayer to optical fibers
10 and inner spaces such as capillaries will likewise
protect the inertness of the glass surface to acidic and
basic attack and to mechanical degradation. Capillary
tubes thus treated are useful in capillary chromato-
graphy and capillary electrophoresis.

15 Of particular interest is the embodiment
wherein a surface comprising zirconium oxide (per se or
alloyed) is treated in accordance with the present
invention to provide protection from the aggressive
environment to which the zirconium-based materials are
20 exposed when they are used as moderators in pressured-
water nuclear power reactors. Preferred groups to
provide on such an oxidic surface are lower alkyl, such
as methyl, and di-dihydroxy lower alkyl, such as $\text{HOCH}_2\text{-}$
 $\text{CH(OH)-CH}_2\text{-}$.

25 As indicated, the monolayer is formed of
silicon atoms bound to the substrate surface and
connected to each other through single oxygen atoms. In
addition, the monolayer is characterized in that it is
substituted with the first and second hydrocarbyl
30 substituents described herein. Each of the silicon
atoms forming the monolayer is substituted with either a
first hydrocarbyl substituent or a second hydrocarbyl

1 substituent. In the broadest aspect of the present
invention, there may be regions of the monolayer in
which the first hydrocarbyl substituent predominates,
even to the exclusion of the second hydrocarbyl
5 substituent, and vice versa. However, in the preferred
embodiment the first and second hydrocarbyl substituents
are both distributed essentially uniformly across the
surface of the monolayer. While it will be recognized
that totally unvarying distribution of the first and
10 second substituents on the monolayer may not be
achieved, the product will generally preferably be
characterized in that each of the first and second
substituents are distributed essentially uniformly, or
as nearly uniformly as possible, on the surface of the
15 monolayer. In that way, the relative proportions of the
first and second substituents will be essentially
constant at any region on the monolayer.

The first and second hydrocarbyl substituents
are preferably selected to optimize the property or
20 properties desired of the product which will bear the
monolayer, and to ensure the provision of a protective
coating to the surface of the article. In the aspect of
the present invention in which the desired property is
the ability to carry out effective chromatographic
25 separation when the article is used as a packing
material for, e.g., HPLC or other gas-phase
chromatography, the first hydrocarbyl substituent should
be one which assists in providing chromatographic
separation when bound to a chromatographic support.
30 Examples of such substituents will be familiar to those
conversant with the field of chromatography, and are
indeed quite numerous. Examples include phenyl;

1 epoxide; alkyl, containing from 1 to 60 carbon atoms in
the longest chain, preferably 1 to 30 and more
preferably 3 to 18 atoms in the longest chain;
monounsaturated alkylene containing 2 to 60 carbon atoms
5 in the longest chain; or derivatives in which alkyl or
monounsaturated alkylene containing up to 60 carbon
atoms contains one or more (preferably up to 12) hetero
linkages such as -O-, -N(R)-, -S-, -C(O)-, -SO₂-,
-C(O)O-, -OC(O)-, -C(O)N(R)-, or -N(R)C(O)-. The
10 phenyl, alkyl and alkylene may optionally be substituted
with one or more of hydroxyl, halogen (particularly
fluorine, chlorine or bromine, especially
fluorocarbons), cyano, nitro, -COOH, -SO₃H, -N(R)(R),
-R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, wherein R¹ and
15 R² are each alkyl, alkoxy or alkylene containing up to 6
carbon atoms, and preferably methyl, ethyl, methoxy or
ethoxy; or straight or branched lower alkyl containing
up to 6 carbon atoms (which lower alkyl may be
substituted with any of the foregoing substituents),
20 wherein R at each occurrence is hydrogen or alkyl
containing 1 to 6 carbon atoms. Thus, -N(R)(R) can be
amino, monoalkylamino, or dialkylamino. Thus, exemplary
functional groups include diol (such as
HOCH₂-CH(OH)CH₂-), polyamine, carboxylic acid, sulfonic
25 acid, and (N-trimethoxysilylpropyl) polyethyleneimine.

A preferred first substituent is alkyl
containing 2 to 24 carbon atoms, and more preferably
octadecyl. Preferred embodiments in which the alkyl
chain has a substituent are those in which the
30 substituent is in the omega-position. Another preferred
first hydrocarbyl substituent has terminal ethylenic
unsaturation. Examples include CH₂=CHCH₂-, and more

1 generally $\text{CH}_2=\text{CH}-(\text{CH}_2)_{1-24}$ -. The unsaturated group is
useful in that other molecules that react with $-\text{CH}=\text{CH}_2$
groups can be attached to the hydrocarbyl substituent at
that site. Epoxide groups and hydride groups, when
5 present attached to the hydrocarbyl substituents, can
also serve as sites to which other molecules and
functional groups can be attached. Examples of such
molecules include ones that impart hydro-phobicity or
color, or which serve as cladding for the surface of a
10 glass filament fiber optic transmission line. Examples
of the latter include C_1 - C_6 acrylates and methacrylates.

The second hydrocarbyl substituent can also be
any of the foregoing substituents, provided that the
second hydrocarbyl substituent is shorter than the first
15 hydrocarbyl substituent. Preferably, for chromato-
graphic applications, the second hydrocarbyl substituent
is sufficiently shorter than the first such that a
chromatographic support prepared in accordance with the
present invention having a given first hydrocarbyl
20 substituent is essentially undistinguishable in its
chromatographic properties from a conventional silica
gel support to which is grafted the same given first
hydrocarbyl substituent. When the first substituent is
 C_{12} - C_{24} alkyl, the second substituent is preferably
25 alkyl containing 1 to 6 carbon atoms and more preferably
propyl. When the first hydrocarbyl substituent is
relatively short, i.e., alkyl containing up to 6 carbon
atoms, or phenyl, the second hydrocarbyl substituent is
preferably a shorter alkyl chain (optionally substituted
30 as described above) or may simply be hydrogen.

In applications of the present invention other
than the preparation of chromatography supports, the

1 first and second hydrocarbyl substituents can be chosen
as appropriate to provide any other desired properties
such as abrasion resistance, translucency, transparency,
5 refractive index, light reflectivity (e.g., outside a
fiber optic line), hydrophilicity, hydrophobicity, or
rheology (for instance, of treated minerals or pigments
in an emulsion or in an aqueous or non-aqueous liquid
preparation). In all events, the monolayer prepared in
10 accordance with the present invention will impart the
product with the desired ability to resist chemical
degradation in acidic and basic environments. The
second hydrocarbyl substituent is preferably one which
maximizes the ability of the monolayer to prevent
penetration of acidic and basic substances and ions to
15 the product surface. Preferred second hydrocarbyl
substituents are thus alkyl groups containing up to 6
carbon atoms, optionally substituted with halogen
(particularly fluorine) or with C₁₋₃ alkyl.

The relative amounts of the first and second
20 hydrocarbyl substituents on the monolayer are readily
adjustable, and should be selected to provide the
desired properties of the product bearing the monolayer.
For instance, for chromatographic applications it is
generally preferred that the density of the first
25 hydrocarbyl substituent be about 2 to about 3 micromoles
per square meter of silica gel surface, which
corresponds to about 20 percent to about 50 percent of
the surface. This permits the second hydrocarbyl
substituent to "space" the longer substituents from each
30 other while still retaining the desired protection to
the substrate and the desired chromatographic
properties. Accordingly, the mole ratio of first

1 hydrocarbyl substituent to the second hydrocarbyl
substituent on the substrate when it is to be used as a
chromatographic material will preferably comprise about
1:1 to about 1:4. It will be recognized that, depending
5 on the property or properties desired, the mole ratio of
the first hydrocarbyl substituent to the second
hydrocarbyl substituent can range from as low as below
1:100 to as high as 100:1, or higher, although the
beneficial effects of the second hydrocarbyl substituent
10 "spacing" the first hydrocarbyl substituents from each
other are less pronounced as the ratio of first to
second hydrocarbyl substituents exceeds about 1:1.

As set forth more fully hereinbelow, the
relative ratios of the reactants employed to form the
15 desired monolayer have to be adjusted so as to provide
the desired ratio of substituents on the monolayer,
taking into account the fact that the reactants will
usually react with the substrate at different rates.
For instance, a smaller reactant such as
20 propyltrichloro-silane reacts more quickly (and thus
more of it reacts in a given period of time) than n-
octadecyltri-chlorosilane. Thus, because of the
differing reaction kinetics of each reactant, the ratio
of one to another before reaction will usually not equal
25 the ratio of one to another on the monolayer following
reaction. The determination of the relative amounts of
each reactant to use, in order to obtain a given ratio
of chain lengths on the monolayer, is a straightforward
matter for any particular choice of substrate and
30 hydrocarbyl substituents.

Preparation of articles bearing the monolayers
described herein is straightforward. The article having

1 surface oxygen is preferably treated to remove
extraneous materials which might interfere with the
bonding of the silane reagent to the available oxygen.
The surface of the article needs to be hydrated, as free
5 water is essential to achieving the desired reaction
between the silane and the surface oxygen. However, the
surface need not and should not carry liquid water in
amounts that would interfere with the desired
interaction between the silane and the surface oxygen.

10 It has been determined that the amount of
water present on the substrate surface affects the
hydrocarbyl group density that is obtained upon the
ensuing reaction, and that excessive amounts of reagent
water lead to decreased hydrocarbyl substituent density.
15 Accordingly, it is highly preferred that the amount of
water present at the surface be that which affords the
densities of 7 or greater, and more preferably 8 or
greater, micromoles of hydrocarbyl substituents per
square meter of substrate surface. That amount of water
20 is generally about equal to the amount (on a mole basis)
required by the silane reagents employed to form the
monolayer. Adequate hydration can be provided by
cleaning and drying the surface of the article to be
treated and then exposing it to a humid atmosphere so as
25 to allow a surface monolayer of water vapor to form on
the article. Alternatively, adequate hydration can be
provided by adding a known, pre-calculated amount of
water to a polar solvent in which the hydrocarbyl
substituents are provided to the reaction site.

30 One technique for applying the monolayer
employs reactants in a liquid phase. According to this
procedure, a solution of silanes of the formula R^1SiX_3

1 and R^2SiX_3 , is formed in a solvent which is inert to both
of these silanes and to the article with which the
reaction will be carried out. In the foregoing
formulas, R^1 is the first hydrocarbyl substituent, R^2 is
5 the second hydrocarbyl substituent and X is a leaving
group which is preferably chlorine, methoxy, or ethoxy.
(If the second hydrocarbyl desired is hydrogen, the
corresponding reactant is $SiHCl_3$.) Suitable solvents
include alkanes which are liquid at room temperature and
10 atmospheric pressure, such as n-hexadecane. The solvent
is preferably scrupulously anhydrous, to prevent
premature reaction of the silane with any trace amounts
of water.

Then, the solution is applied to the surface
15 on which formation of the monolayer is desired.
Depending on the nature and size of the article, it can
simply be immersed in the solution under a suitable
inert gas blanket to ensure that no atmospheric water
vapor interferes with the desired interaction between
20 the article, the reagent surface water, and the silanes.
No special catalysts or extreme reaction conditions need
be observed; the silanation reaction generally proceeds
to completion in a matter of hours. In general, it can
be expected that slightly raising the temperature of the
25 reaction mixture will accelerate the completion of the
reaction. The progress of the reaction can be followed
in any of a number of conventional ways, for instance by
monitoring the formation of HX in the solution; when the
concentration of HX stops increasing, the consumption of
30 the silane has ceased.

Following the completion of the reaction, the
thus treated material is removed from the solution,

1 washed, and dried. It can then be handled and treated
in accordance with techniques currently employed with
analogous materials to which the monolayer has not been
applied in accordance with this invention. For
5 instance, silica gel treated in this manner can be
incorporated into an appropriate column to permit its
use as a chromatographic packing material. Then, any
mixture desired to be treated or analyzed chromato-
graphically is simply applied to the column in a wholly
10 conventional manner.

The monolayer can also be applied in the vapor
phase. The surface to be treated (following surface
cleaning, as described above) is contacted with a vapor
which comprises the silanes of the formula R^1SiX_3 and
15 R^2SiX_3 , wherein R^1 , R^2 and X are as defined above. The
vapor may consist entirely of these silanes, or it may
contain, in addition to those silanes, any other reagent
intended to be reacted with the substrate surface; and
the vapor should contain sufficient reagent water vapor
20 in appropriate relative amounts as described herein to
provide the desired high density of hydrocarbyl group
coverage. Also, the vapor may contain as well diluents
or carrier gas components which will not react with the
silanes nor with the surface. The vapor should be free
25 of components which, if present, would undesirably react
with the surface and interfere with the formation of the
desired surface layer.

The silanes can be applied by placing the
substrate in a chamber containing the silanes.
30 Alternatively, for a substrate such as a fiber optic
filament, the fiber can be drawn through such a chamber
under conditions providing sufficient temperature,

1 circulation of the silanes, and residence time in the
chamber, such that the desired reaction at the substrate
surface occurs. Such an application technique permits
faster treatment times than applications from a liquid,
5 because there is much less residual drag than is
inherent in drawing a fiber through a liquid. This
technique also permits incorporation of other components
that would also be desirably applied to the surface.
The vapor-phase reaction is preferably carried out at
10 temperatures of about 100°C to 140°C.

One advantage of the invention is thus that
the chain length densities can be arbitrarily varied,
depending on the final product and properties desired.
Another advantage is that the final product exhibits no,
15 or a reduced number, of residual geminal silanols (i.e.
silicon with two hydroxyl groups).

When the treated material is a mineral or
pigment, it can be subdivided and added into other
desired compositions such as paints, cosmetic
20 preparations, and the like.

It has also been determined that the
hydrolytic stability of monolayers applied in accordance
with this invention can be enhanced by a technique which
converts residual silanol groups present to other more
25 inert species. Such silanol groups (i.e., -Si-OH
groups) may be present on the monolayer or on the
substrate itself and are convertible at either site.

The hydroxyl group of the silanol group is
converted via a two-step process to a group Z wherein Z
30 is connected to the silicon atom by a Si-C bond. In the
first step, the -OH group is replaced by a halide,
preferably -Cl. In the second step, the halide is

1 replaced with alkyl, preferably C₁-C₆ alkyl and more preferably methyl.

The first step is advantageously carried out by halogenating the silanated material bearing hydroxyl-
5 substituted silicon atoms with a halogenating agent, under anhydrous conditions. A preferred halogenating agent is thionyl chloride (SOCl₂). Then, the halogenated intermediate that is thus formed is reacted with an alkylating agent, again under anhydrous
10 conditions. The preferred alkylating agent is a Grignard reagent, preferably an alkylmagnesium bromide such as CH₃MgBr. The reaction product should then be washed to remove salt byproducts.

This procedure is particularly useful for
15 "endcapping" material containing a surface of silicon and oxygen atoms, and material comprising a polysiloxanyl monolayer such as that obtained with the present invention, to ensure the absence of Si-OH groups on such surface or monolayer. The Si-C bond that is
20 created is stable to hydrolytic attack.

The present invention will be illustrated in the following example. This example should be interpreted as illustrative, and not as imparting limitations to the scope of the present invention.

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EXAMPLE 1

Preparation and characterization of a mixed, horizontally polymerized bonded chromatographic phase:

5 I. Preparation procedure for chromatographic packing material:

A solution was prepared by mixing n-octadecyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$) and n-propyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_2\text{SiCl}_3$) in a 4:1 volume ratio in
10 anhydrous n-hexadecane. (Several other volume ratios of the octadecyl to the propyl derivatives in solution had been used, including 1:1, 2:1, and 3:1, 8:1 and 3:2; the 4:1 gave the chromatographic behavior that most closely resembled that of a conventional chromatographic
15 material.) The n-hexadecane has been made anhydrous by passing it through a column of dry alumina and silica in a glove box having an atmosphere of nitrogen. The reagent was kept under the glove box in preparation for the reaction with 50 μm silica gel particles. These
20 silica particles were cleaned in boiling, concentrated nitric acid and rinsed with ultrapure water, and dried under nitrogen. The surface of the silica particles was hydrated by exposure to the vapor of ultrapure water for one hour. After this exposure period, the n-hexadecane
25 solution was mixed with the silica particles and allowed to react at room temperature, under nitrogen, for a period of one day. The resulting bonded silica particles were cleaned by pouring off the n-hexadecane and rinsing sequentially with n-hexane, toluene,
30 acetone, and methanol. Some of this material was used to pack a chromatographic column for subsequent study with a commercial high performance liquid chromatograph,

1 and some of the material was submitted for analysis by
NMR spectroscopy.

II. Characterization of the material by NMR
spectroscopy:

5 ✓ A. ^{13}C NMR

✓ The ^{13}C NMR spectrum of the material was
obtained for the purpose of determining the relative
amounts of the C_{18} and C_3 chains attached to the
surface. The peak for the first carbon from the silicon
10 atom, which is common to both the C_3 and C_{18} chains, was
four times as large as the peak for the eighteenth
carbon from the silicon, which is only contained in the
 C_{18} chains. The ratio of the peak areas revealed
approximately a 3:1 mole ratio of $\text{C}_3:\text{C}_{18}$ on the surface.
15 This finding confirmed that the propyltrichlorosilane
reacted more quickly with the substrate surface than the
octadecyl silane. This mole ratio would be expected to
provide, in the silica gel provided with a monolayer
according to this invention, the same chromatographic
20 behavior as a monomeric phase. The reason is that,
assuming the total coverage of C_{18} and C_3 is about 7
 $\mu\text{mol}/\text{m}^2$, a 3:1 mole ratio of $\text{C}_3:\text{C}_{18}$ would correspond to
a C_{18} coverage of about 2 $\mu\text{mol}/\text{m}^2$. This is a typical
coverage for a silica gel chromatographic material to
25 which has been bonded individual C_{18} chains.

B. ^{29}Si NMR

The ^{29}Si NMR spectrum of the material was
obtained for the purpose of determining the amounts of
unreacted Si-OH bonds in the horizontally polymerized
30 monolayer. Trifunctional silanes can give rise to
multiple -OH groups on silicon atoms after the reaction
is complete, and these groups can have a deleterious

1 effect on the chromatographic performance. Providing a substituted monolayer in accordance with the present invention should result in fewer of these groups.

5 Spectra were obtained for the material produced in Part I and for a conventional polymeric phase (Sander and Wise, Anal. Chem. Vol. 56, pp. 504-510 (1984). Based on interpretations published in the chemical literature, the peaks on the spectra that were obtained were assigned to the entities $R-Si-(OH)_2$, $R-Si-OH$ and $R-Si-O-$
10 Si . A comparison of these two spectra confirmed that the product from Part I has fewer groups with the structure $R-Si-(OH)_2$ than does the conventional polymeric phase.

III. Chromatographic performance of the material:

15 A. Retention behavior

Chromatograms were obtained using material according to the present invention, prepared in accordance with Part I, and for a conventional monomeric phase comprising the reaction product of chlorodi-
20 methyloctadecyl silane and silica gel refluxed in toluene and end-capped with chlorotrimethyl silane. The mobile phase was 70% methanol in water at 30°C, and the solutes toluene and benzyl alcohol were used. The chromatograms showed that the retention behavior is very
25 similar for the two columns. This result is consistent with the NMR data.

Chromatograms were also obtained for the solutes benzo(a)pyrene and phenanthro[3,4-c]phenanthrene using a mobile phase of 85% acetonitrile in water. The
30 retention order of these solutes has been reported to be reversed for monomeric and polymeric phases, thus constituting a test of whether the mixed phase has

1 selectivity akin to a monomeric or polymeric phase. The
retention order observed for the mixed column was the
same as that for the monomeric phase and reversed from
that of the polymeric phase. (In a "polymeric" phase,
5 the silica gel is reacted with one compound of the
formula SiCl_3R under conditions such that a small amount
of water is intentionally introduced to cause a small
amount of polymerization of the silane. The resulting
chains polymerize to form a chain of repeating $-(\text{Si-O})-$
10 units which extends from the silica gel surface; no
monolayer is present as in the present invention.) This
result observed supports the idea that the chromato-
graphic phase prepared in accordance with the present
invention provides the type of selectivity that a
15 monomeric phase provides.

B. Reproducibility

To determine the reproducibility of the
preparation method, the procedure was followed for
another batch of silica and silane reagent mixture. No
20 special care had been taken to pipette exactly the same
ratio of silanizing reagents as had been used for the
previous batch, nor was special care taken to prepare
quantitatively the same mobile phase composition.
Instead, graduated cylinders were used for dispensing
25 reagents and solvents. Chromatograms for the separately
prepared batches were obtained; the averages of 5 runs
for each column were within 1% of one another.

C. Stability to acid hydrolysis

To test the stability toward acid hydrolysis,
30 a procedure used by a manufacturer of acid-stable
chromatographic phases was adopted. The mobile phase
composition was a mixture of 0.5% trifluoroacetic acid

1 in acetonitrile, designated as A, and 0.5%
trifluoroacetic acid in HPLC water, designated as B,
with the percentages of A and B indicated in the Table
below. The flow rate was 2.0 mL/min and the temperature
5 was 50°C. The cycle used is tabulated below.

T0220X

	<u>Time (min)</u>	<u>(A)</u>	<u>(B)</u>
(1)	0.00-6.49	72%	28%
(2)	6.50-15.99	85%	15%
(3)	16.00-25.99	100%	0%
10 (4)	26.00-49.99	0%	100%
(5)	50.00-59.99	72%	28%

Loop back to 0.00 min.

A 100-hour run (which is 100 cycles of the tabulated
loop) for the column according to the present invention
15 prepared in accordance with Part I was completed for the
tabulated programming of trifluoroacetic acid in water
and acetonitrile, using the solute benzo(a)pyrene.
Below is a tabulation of the retention time of
benzo(a)pyrene after the specified number of hours of
20 mobile phase cycling.

T0221X

	<u>Hours</u>	<u>Retention Time</u>
	0	5.65
	24	5.70
	48	5.68
25	72	5.69
	96	5.67

These data show that there is no change in retention
time within the 1% noise on the measurement. The run
was continued for another 24 hour period and there was
30 still no change in the retention time. This stability
is higher than any known C₁₈/silica phase, including
both monomeric and polymeric phases.

1 D. Stability to base hydrolysis

Base hydrolysis is the most severe limitation of silica-based chromatographic phases. The stability to base hydrolysis of the column according to the present invention prepared in accordance with Part I was compared to that of the aforementioned conventional monomeric phase, which was end-capped with chlorotrimethylsilane to provide maximum stability. The mobile phase composition was 5% n-propanol in water, with NaOH added to make the pH approximately 12. (A pH of 12.4 at room temperature was measured using a pH meter.) The following cycling was used to monitor the stability to base hydrolysis. The flow rate was 2.0 mL/min and the temperature was 50°C.

- 15 (1) 20 minutes of 5% n-propanol at pH of nominally 12.
(2) 18 hours of HPLC water
(3) 20 minutes of 70% methanol in water
(4) Inject benzyl alcohol and toluene in 70%
20 methanol in water; measure retention time
(5) Loop back to Step 1

The capacity factors (k') of benzyl alcohol and toluene after each cycle showed that the monomeric phase degraded more quickly than the phase according to the present invention. More significantly, during the second run of the base solution (step 1) for the monomeric column, the mobile phase was observed to become a milky color, which indicates that the silica substrate began dissolving. The pump pressure was observed to be increasing, therefore, the cycling was discontinued. These same observations were made for another monomeric column. By contrast, no such

1 substrate degradation was observed for the mixed phase
over the entire period of the study which included three
loops through the cycle. Chromatograms could thus be
obtained from a column according to the present
5 invention even after exposure to a substantial volume of
base.

Additional experiments showed that endcapping
of the mixed phase provided further improvement in
stability toward base hydrolysis. The preferred
10 endcapping reagent is chlorotrimethyl silane;
chlortri(isopropyl) silane, for example, can also be
used.

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